

# **DEVELOPMENT OF A TOOLBOX USING CHEMICAL, PHYSICAL AND BIOLOGICAL TECHNOLOGIES FOR DECONTAMINATION OF SEDIMENTS TO SUPPORT STRATEGIC ARMY RESPONSE TO NATURAL DISASTERS**

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## **ABSTRACT**

Environmental technologies, developed by the Department of Defense for life cycle management of energetic materials can be leveraged for use in pollution prevention and remediation of a broad range of compounds and impact scenarios (Downey et al., 2006). The Environmental Security Initiative (ESI) and Natural Disaster Response Initiative (NDRI) are examples of programs developed by the US Military to transition and adapt technologies developed for energetics to the clean-up of environmental and strategic resources resulting from new pollution threats caused by natural disasters and potentially, terrorist activities. This paper describes preliminary testing results for physical, chemical and biological treatment methods transitioned from remediation of energetic impacted materials to remediation of sediments deposited by hurricane Katrina. Results were combined into a data-base toolbox and used to develop a Venn diagram/decision matrix for rapid selection and application of appropriate remediation technologies in emergency situations. Technologies considered include stabilization or emulsification (of metals, organic contaminants, and pathogens); biological treatment (for pathogen destruction, organic degradation and material recycling); and chemical oxidation (for destruction of organic and inorganic chemicals, and pathogens).

Results of this preliminary study show a five fold reduction in lead concentration in sediments treated with chemical agents such as lime, asphalt based emulsion and tall oil pitch (also known as pine pitch) emulsions. The application of a chemical disinfectant to eliminate pathogens, however, reduced the effectiveness of the emulsifier by about 8%. Leachable organics were reduced

3 to 6 fold when treated with the emulsifier and appeared to be independent of the chemical disinfectant. Biological treatment potential (as an alternative to chemical disinfection) was tested using soil microcosms and respirometry to determine diesel range and total organic compound degradation. These tests were used to generate parameters such as oxygen uptake rate, compound degradation and amendment requirements for design of a composting based remediation strategy. Based on these data, the rate of oxygen uptake by alkane degrading bacteria under test conditions, begins after a lag of about 20 hours and peaks at about 45 to 50 mg/kg/hr. Based on stoichiometry this is equivalent to about 15 mg of hydrocarbon degraded/kg impacted sediment/hr or about 265 gallons removed from 1 ton of soil per year. Results of chemical, physical and biological testing are summarized into a decision matrix for rapid feasibility analysis and remedial technology selection. The work reported here is a preliminary report of on-going research.

As a result of this project, the US Army is better prepared to directly support improved emergency remediation activities implemented by the Joint Services, Department of Homeland Defense, civil authorities, and/or private contractors.

## **1. INTRODUCTION**

A state of emergency was issued for Louisiana on August 28, 2005 as hurricane Katrina advanced towards the Louisiana coast. Katrina touched shore on August 29, 2005 resulting in one of the worst natural disasters in US history. Due to the massive extent of the disaster, more than 50,000 soldiers from many US Army National Guard units were mobilized to provide emergency services to the affected area. The readiness of other units was disrupted

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due to the damage caused in the area, hindering orderly mobilization. In addition, the Army Corps of Engineers marshaled teams to assess infrastructure damage and develop remedial plans. The total impact to the Army is difficult to calculate, but it includes the loss of units for potential overseas rotation as a result of their diversion to relief duties as well as the damage to Army infrastructure, extended time to restore such infrastructure, and inability to mobilize units representing the affected areas.

While Guard units were assisting in restoring order and providing immediate relief, and Engineer teams were assessing damage and performing temporary repairs, civil authorities were issuing a number of declarations, administrative orders and waivers for local governments handling Katrina debris (Eliah, 2006). These declarations were issued by the Louisiana Department of Environmental Quality (LDEQ). While LDEQ declarations, administrative orders and waivers provide flexibility and innovation for debris handling and management, LDEQ must still adhere to its mission of protecting the state's environment to the fullest extent possible (Louisiana Department of Environmental Protection, 2006). To assist these types of efforts, the Natural Disaster Response Initiative (NDRI) was created. The NDRI was developed by the US Military, through the combined efforts of the Army Corps of Engineers, the Engineering Research and Development Center (ERDC) and the Army Research Development and Engineering Command- (ARDEC). The purpose of the initiative is to apply and adapt advanced environmental technologies developed for defense purposes to greatly speed up natural disaster clean-up and restoration (Conner et al., 2006). This effort is consistent with three specific purposes of the Army's current environmental strategy including; (1) reducing costs and minimizing impacts so the Army can do more, and do it better; (2) enhancing human health, safety, and well-being; and (3) being an active citizen within our communities as well as a good neighbor. This project demonstrates and integrates three technologies into an application toolbox for rapid decision making, technology targeting, and treatment initiation for sediments impacted by a mixture of inorganic, organic and biotic contaminants. Technologies include emulsion treatment for stabilization of metals, organic contaminants, and bacteria; biological treatment for pathogen destruction; and organic recycling and chemical oxidation for organic destruction. As a result of this project, the US Army is prepared to directly support improved emergency remediation activities by the Joint Services, Department of Homeland Defense (US Coast Guard), civil authorities, and private contractors while implementing its official environmental strategy.

## 2. METHODS/MATERIALS

Material evaluated for development of the NDRI Technology Toolbox consisted of sediments deposited by hurricane Katrina in St. Bernard Parish, Louisiana (Data Report DNC # KR1-P). According to this report Arsenic exceeded the Louisiana DEQ background concentration. Iron exceeded the screening level for residential soils. Dieldrin (pesticide) was detected above its chronic screening level. Polynuclear aromatic hydrocarbons (oil and grease) such as benzo(a)pyrene were detected above chronic (long term-measured in years) screening levels. Levels of diesel and oil range organics exceeded the Louisiana standards for residential exposures by approximately 15 and 5 times respectively. Health guidance indicates that contact with these oily sediments should be avoided and may result in skin irritation and neurological effects such as headaches and dizziness. Approximately 10 gallons of Katrina deposited sediment was obtained for this study. Material was blended by hand and sub-sampled as required for testing. Emulsion treatment for stabilization of metals, organic contaminants and bacteria was tested by lime drying the sludge (5% quick lime) followed by emulsion treatment using three basic types of emulsions provided by Encapco Technologies, LLC. The emulsions were prepared using three different levels of disinfectants. Treatments were performed by adding 3% by weight of each emulsion with the lime dried sludge. Controls consisted of non-emulsified lime treated and untreated material. After 48 hours the test materials were extracted using Toxicity Characteristic Leaching Procedure (TCLP) and an 18 hour extraction in deionized water. Although 10 metals were screened, only lead had concentrations within reporting limits.

Biological treatment potential was tested using soil microcosms and respirometry (N-Con Comput-Ox-4R, model 244). The respirometer measures oxygen demand in water or soil samples and is commonly used by government, universities, and industry to conduct reliable, long term studies of biodegradability, bioremediation, and toxicity of liquid and solid samples. The Comput-OX 4R is a 4 reactor unit with no stirring modules or temperature controlled water bath. This provides a low cost respirometer for soil or compost work which requires no stirring. The 4 individual ports were connected to airtight containers constructed as soil microcosms to measure oxygen uptake during simulated compost studies. For this analysis Katrina deposited sediment was mixed with 25% wood chips, 2.5% fertilizer and enough water to result in a 50 to 60 % moisture content. Material was mixed thoroughly and inoculated with approximately 2 grams of hydrocarbon degrading bacteria (Novozyme, Inc.). Material was placed into a test reactor and oxygen uptake measured over a 1 week period.

### 3. RESULTS

Sediments deposited by Hurricane Katrina have been extensively sampled and characterized by the LDEQ. Material can be separated into three general categories non-biodegradable inorganics (metals and pesticides), biodegradable organics (petroleum hydrocarbons), and biotics (pathogens). Material evaluated for development of the NDRI Technology Toolbox consisted of petroleum impacted sediments collected from St. Bernard Parish, Louisiana.

Biological treatment potential was tested using soil microcosms and respirometry to determine diesel range and total organic compound degradation. An oxygen uptake curve obtained for Katrina deposited sediment is provided in Figure 1.

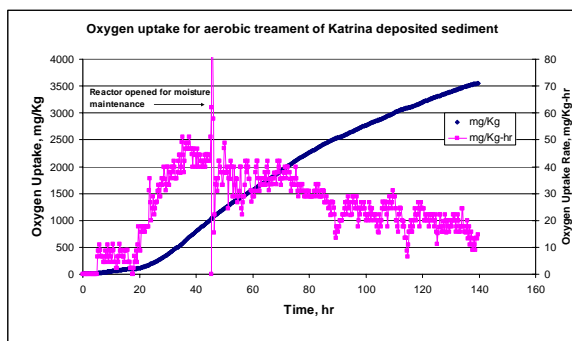


Fig.1. Oxygen uptake curve Katrina deposited Sediment

Oxygen uptake results were used to generate parameters such as compound degradation rate, and amendment requirements for design of a composting based remediation strategy. Composting is an EPA approved technology used to stabilize municipal waste solids. It characteristically is an aerobic microbial based technology that results in a high temperature curing stage suitable for treatment of vegetative waste, sediment and municipal sewage. The target temperature and sustained duration during curing are designed to kill pathogens, rendering the resultant product safe for reuse as a fertilizer or soil amendment. Based on these data, the rate of oxygen uptake by alkane degrading bacteria begins after a lag of about 20 hours and peaks at about 45 to 50 mg/kg/hr. Based on stoichiometry this is equivalent to about 15 mg of hydrocarbon degraded/kg impacted sediment/hr or about 265 gallons removed from 1 ton of soil per year.

Chemical/physical treatment data show that treatment with lime alone was effective at reducing lead concentrations about five fold. In most cases, the emulsion treatments reduced lead levels further. Both

ACCS (Asphalt based emulsion) and TOP (Tall Oil Pitch emulsion) were effective in reducing leachable lead concentrations, but TOP performance was superior to ACCS. A proprietary disinfectant was added to the emulsifier at 1%, 3%, 5% and 7.5% by weight. In both ACCS and TOP tests disinfectant added at 7.5% appeared to negatively affect performance of the emulsifier. Figure 2 illustrates the emulsification potential for lead impacted soil. Figure 3 illustrates the effect of emulsification on leached organic content of soil. Leached organic content of the material was reduced 3 to 6 fold with the TOP treatments performing best. Wet conditions of the material likely interfered with emulsification. Addition of a disinfectant did not appear to impact emulsification of the organics.

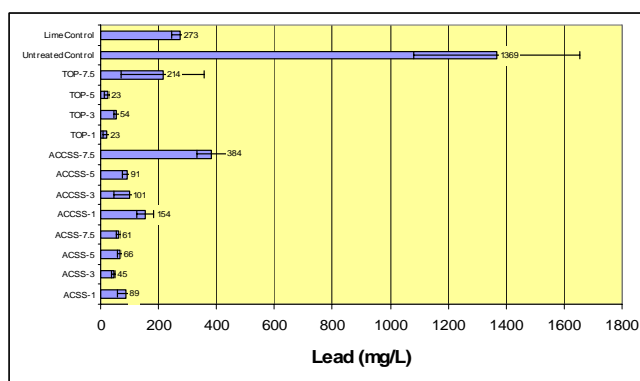


Fig.2. Reduced leaching of lead due to emulsification

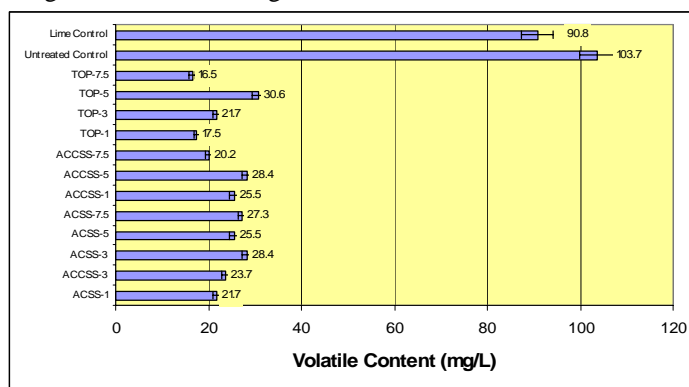


Fig.3. Reduced leaching of organics due to emulsification

Leachate from the untreated control, lime control, and the TOP-5 were analyzed for heterotrophic bacteria. The Table presented below indicates that a reduction in microbial population counts can be achieved using both quick lime and the TOP emulsifier using 5% disinfectant. Results are provided in Table 1.

Table 1: Bacteria level after various treatments	
Treatment	Viable Bacteria (colony forming units per mL)
Untreated Control	12,000
Lime Control	4,000
TOP 5	2,200

A Venn diagram was developed for use as a preliminary matrix tool for technology application decisions. Venn diagrams are illustrations used in set theory to show mathematical or logical relationships between different groups of things or sets (Wikipedia). The Venn diagram (process devised by and named for John Venn, 1834-1923) consists of two or more circles, each representing a specific group. A simplified Venn diagram for Katrina impacted sediments is provided in Figure 3.

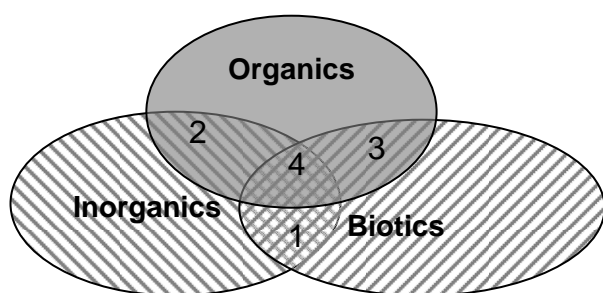


Fig. 4. Venn diagram illustrating technology application overlap for Katrina deposited sediments

This diagram illustrates overlap areas 1 through 4 representing mixtures of (1) pathogens and inorganic metals (2) metals and hydrocarbons (3) hydrocarbons and pathogens and (4) pathogens, metals and hydrocarbons. This study has demonstrated that stabilization/disinfection can be used for sediments characterized by area 1, stabilization alone can be used for area 2, composting or stabilization/disinfection can be used for contaminants in area 3 and stabilization/disinfection can be used for materials characterized by area 4. All remediation technologies described are ex-situ and can be implemented using existing soil agitation equipment that aggressively turns soil to combine treatment reagents with the sediment. An example of such equipment is depicted in Figure 5.



Fig. 5. Soil turner for application of emulsification agents, disinfectants or compost amendments.

## 4. CONCLUSIONS

Chemical, physical and biological technologies are available through the US Army to contain and treat sediments containing a mixture of organic and inorganic contaminants. Technologies can be used independently or in combination to effectively decontaminate and recycle impacted sediments. The LDEQ has an established debris management plan that includes vegetative, oil or hazardous waste impacted material, and flood water sediment. Current plans identify chipping and grinding sites, burn sites, and land fill disposal of sediments. The LDEQ will consider reasonable waiver requests in order to affect rapid and environmentally safe waste treatment goals. The technologies developed and demonstrated in this project meet the waiver request requirement and can be used to reduce current burn and landfill diverted materials. The coordination and cooperation among civil and military authorities in this effort has provided options for remediation not hitherto available and provides remediation participants greater flexibility for rapid restoration. The use of military authorities for disaster relief has a long history in this country. Such missions are an integral part of some Army operations, particularly for National Guard Units. However, disruption of these units and their infrastructure (armories, equipment, transportation assets, etc.) caused by natural disasters or the diversion of these units as a result of mobilization required to restore order or to provide initial humanitarian relief, reduces their readiness to respond to world wide Global War on Terror operations. A further effect of these disasters is the potentially huge environmental impact, causing additional delays in returning military and civil operations to normal. To improve the response to the environmental impacts and to support the Army's environmental strategy, a toolbox of rapid remediation techniques has been developed and demonstrated. Improved emergency remediation activities by the Joint Services, Department of Homeland Defense (US Coast Guard), civil authorities, and private contractors are now

possible using these techniques. The rapid restoration of normal operations to affected areas will not only provide a tremendous benefit to the civil sector, both humanitarily, sociologically, and economically, but also to the military sector, returning affected units much sooner than before to the high state of readiness demanded in today's world geo-political environment.

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